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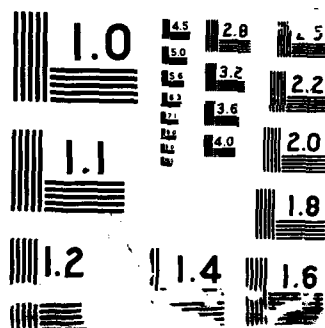
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Blends of Crystallizable Polybutadienes

by

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## Blends of Crystallizable Polybutadienes

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### Abstract

This report provides baseline data on two crystallizable polybutadiene homopolymers (trans 1,4 PBD and syndiotactic 1,2 PBD) and on 50/50 weight percent homopolymer blends. Blends were prepared by a solution casting method discussed in the report. Results of molecular characterization and thermal analysis experiments are presented.



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## INTRODUCTION

This progress report describes work done to date on the topic "Blends of Crystallizable Polybutadienes: Morphology Control via Diblock Addition in the Melt". The objectives of the research are to determine: a) the compatibility and behavior of binary blends of crystallizable syndiotactic 1,2 and trans 1,4 polybutadienes (PBD), and b) the effect of amorphous 1,2/1,4 PBD diblocks on the crystallization and phase separation of these blends. Work to date has focused on characterization of the individual homopolymers and of 50/50 (wt%/wt%) blends of the homopolymers. We have obtained IR, NMR, and DSC data for the homopolymers. Conditions for spincast solution blending of these materials were optimized and the resultant blends were analyzed using DSC.

## HOMOPOLYMERS

The polybutadiene homopolymer samples were obtained in powder form from Dr. A.F. Halasa of Goodyear Tire and Rubber Company in Akron, OH. Both syndio 1,2 and trans 1,4 PBD have a molecular weight of 54.09 grams per repeat unit.

The syndiotactic PBD was made on or before 10/29/85, and was reported by Halasa to have a melting point of 195 C and to have a structure of 90% 1,2 units and 10% 1,4 units as determined by IR. Syndio PBD crystals are orthorhombic and have unit cell dimensions of  $a=10.98\text{\AA}$ ,  $b=6.60\text{\AA}$ , and  $c=5.14\text{\AA}$  (Natta and Corradini, 1956). Heat of fusion of pure syndio is at least 24.6 cal/g (Ashitaka, 1983a).

The trans polymer was made by Zeigler-type catalysis, and was reported by Halasa to have a melting point of 150 C and a structure that is about 90% trans. Trans PBD is polymorphic, having one crystal form below about 75 C that is referred to as modification I (mod I) and a second form between 75 C and the melting point, referred to as modification II (mod II). According to Iwayanagi et al. (1968), mod I crystals are monoclinic with crystal dimensions of  $a=8.63\text{\AA}$ ,  $b=9.11\text{\AA}$ , and  $c=4.83\text{\AA}$ . According to Natta and Corradini (1959), mod I crystals are pseudohexagonal with lattice dimensions  $a=4.54\text{\AA}$  and  $c=4.92\text{\AA}$  and according to Seuhiro et al. (1970),  $a=4.60\text{\AA}$  and  $c=4.83\text{\AA}$ . The transition to mod II is reversible and is characterized by a 9% increase in volume (Natta and Corradini, 1959). Mod II crystals are pseudohexagonal and have dimensions  $a=4.88\text{\AA}$ ,  $c=4.68\text{\AA}$  (Natta and Corradini, 1959) or  $a=4.95\text{\AA}$ ,  $c=4.66\text{\AA}$  (Seuhiro et al., 1970). There is also some disagreement in the literature as to the exact temperatures and enthalpies

associated with the various transitions, as shown in Table 1. To calculate trans PBD crystallinity fractions in our samples, we used Danusso's (1966) values of 40.6 cal/g for the enthalpy of transition between mods I and II and 20.3 cal/g for the enthalpy of melting.

#### BLENDING

Blending of polymers is generally accomplished in one of three ways: 1) mechanical blending of the melt followed by compression molding, 2) solution precipitation followed by compression molding and 3) solution casting directly into films. The last procedure is usually done by slow solvent evaporation onto a flat glass plate. In our lab, however, a spin casting method (Bates et al, 1983) is employed whereby the polymer solution is spun in an aluminum cup. As the solvent is driven off by a stream of nitrogen, a film forms on the cup wall. The wall is lined with Mylar so that the film can then be removed from the cup and peeled from the Mylar.

All but the first technique listed above require solvent for the polymers. Neither the trans nor the syndio PBD samples obtained from Goodyear were soluble in boiling toluene (110 C); syndio (but not trans) dissolves in boiling xylene (140 C). Ashitaka et al. (1983b) used o-dichlorobenzene (bp 177 C) and tetralin (1,2,3,4 tetrahydronaphthalene, bp 207 C) as solvents for syndio PBD at 140 C. Our studies indicate that trans PBD goes into o-dichlorobenzene at about 130 C but separates from the solvent and into a gel-like blob as soon as the temperature drops, making the material difficult to handle. Both homopolymers go into solution well in tetralin: trans at 105 C and syndio at 125 C.

One percent to 1.5% solutions of the homopolymers in hot tetralin (160 C) were poured into a preheated spincasting cup (120 -150 C) and then processed at 160 C. Ethyl 330 antioxidant (1,3,5 trimethyl-2,4,6-tris[3,5-di-tert-butyl-4-hydroxybenzyl]benzene) was added to all solutions in concentrations up to 0.05g/g polymer. Nitrogen purged the cup at rate of 10 SCFH. After 16 hours, the temperature controller was turned off and the temperature decreased to about 40 C, usually after a period of about three hours, the film was removed from the cup and placed in a room temperature vacuum oven for a sufficient time to remove residual solvent. These conditions gave tan-colored trans PBD films and light yellow syndio PBD films. The as-received trans homopolymer powder is slightly off-white in color, thus the tan color of the trans films suggests that the films

oxidized. The syndio homopolymer powder is initially light yellow, so there may be only minor oxidation in these samples. Detailed further investigation into the role of antioxidant in preventing oxidative degradation of processed films is underway.

The syndio films separated from the Mylar during the spin casting process. The trans films, on the other hand, generally stuck to the Mylar and could not be peeled off without ruining the film. These observations suggest that the syndiotactic polymer crystallizes from solution during the casting process, whereas the trans polymer remains an amorphous melt during the casting process and crystallizes later during cooling in the bulk state. To prevent the trans from sticking, we lowered the processing temperature to 120 C, below the melting point of the trans. Keeping all other conditions the same, this change gave trans films which adhere to the Mylar, yet were removable if peeled off slowly and carefully.

Fifty/fifty blends of the two homopolymers cast at both 160 C and 120 C yielded films that stuck to the Mylar yet came off with the aid of a razor blade. The texture and color of these films were intermediate between those of the homopolymer films. Without the aid of microscopy, the morphologies of the blends appeared not to be uniform. Further details await the results of ongoing microscopic analysis.

#### GEL PERMEATION CHROMATOGRAPHY

For the purpose of characterizing the as-received samples, we have attempted to obtain high temperature gel permeation chromatography data on the two homopolymers. A Waters 150C GPC was used at 140 C with tetralin as the mobile phase. No antioxidant was added to the polymer solutions (0.1 to 0.8%).

Results showed that extensive degradation of the polymers occurred in the GPC, to the extent that all elution times were longer than that of the lowest molecular weight polystyrene standard ( $M=2,400$  g/mole).

Successful protection of the chains from degradation during the GPC experiments is a high priority for the forthcoming period of work so that the extent of molecular deterioration during sample processing can be documented and reduced if necessary.



## INFRARED SPECTROSCOPY (IR)

IR was performed to examine the microstructure of the homopolymers. Small amounts of the homopolymer powders were placed between two slides and heated on a hot plate until the polymer melted. The slides were then removed from the heat. Enough polymer was used to ensure a thin film at least 1/2 inch in diameter. When the slides reached room temperature, they were carefully pried apart. The pressed polymers were removed from the slides with a razor blade and taped onto sample holders for the IR spectrometer (Perkin-Elmer, model 727B). To check reproducibility, spectra show were obtained for various positions of the samples. To determine an approximate range of error, each spectrum was run twice on the same sheet of paper.

Our results are in Figures 1b and 2b and are listed in the first column of Tables 2A and 2B for syndio and trans, respectively. Our data agree very well with spectra of Morero et al. (1960, 1962) shown in Figures 1a and 2a and listed in the second column of Tables 2A and 2B for syndio and trans. Other published polybutadiene spectra and data include only certain bands, as listed in the third columns of Tables 2A and 2B. Assignments are found in the Morero papers mentioned above. In the spectrum for syndio, we obtained bands between 2130 and 2330  $\text{cm}^{-1}$  that are not reported in the literature, and our trans spectra show a broad band at 2340  $\text{cm}^{-1}$  that is not documented in the literature. At present we have no explanation for these bands.

A spectrum for a spincast trans film, shown in Figure 2c, gave identifiably trans data; however, some peaks are more pronounced than in the melt-cast trans sample while others are less pronounced.

## NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

$^1\text{H}$ -NMR was performed on 1.5% syndio solutions and 1.0% trans solutions in 307. deuterated tetralin at 150 C and 250 Hz. Syndio samples (2.07%) and trans (1.5%) in tertralin at 150 C were used for the  $^{13}\text{C}$ -NMR. In the absence of an internal standard, the spectra were referenced to the spectrum for tetralin.

In addition to the solvent peaks, we obtained  $^1\text{H}$ -NMR peaks at 2.3, 5.1-5.5, and 7.7 ppm for syndio and 2.2, 5.6, and 7.7 ppm for trans, as shown in Figures 3b and 3c. Table 3 lists our data along with literature values and assignments for both 1,2 and 1,4 PBD. Values that are specifically for syndio 1,2 and trans 1,4 are designated as such in the table. Trans peaks appear farther downfield

than expected and two syndio peaks found in the literature around 1.3 and 5.5-5.6 ppm are not present in our spectra at all. Both PBD samples gave a peak at 7.7 ppm that is not reported in the literature for PBD or tetralin.\* Samples with higher concentrations in perdeuterated tetralin will be examined in an attempt to obtain better data for both  $^1\text{H}$  and  $^{13}\text{C}$ -NMR.

Solid state Magic Angle Spinning (MAS)  $^{13}\text{C}$ -NMR was performed on both homopolymers. The cross polarized, proton decoupled spectra are shown in Figure 4a for syndio PBD and in Figure 4b for trans PBD. Syndio peaks are at 40, 118, and 143 ppm. for the trans PBD, a doublet occurred at 33,35 ppm and at 130,131 ppm. The smaller peaks are sidebands of the latter doublet and appear due to limits in the spinning speed of the sample. These data are listed in Table 4 along with data of Schilling et al. (1984, 1987) and Moller (1984). We found no literature on solid state NMR for syndio PBD, but by analogy to solution  $^{13}\text{C}$ -NMR, we expected four peaks around 39, 41-42, 114, and 143 ppm. We do not have an explanation for the appearance of three peaks in our data on the syndio polymer. The trans PBD doublet at 33,35 ppm can be assigned to aliphatic (methylene) carbons and the doublet at 130,131 to olefinic carbons. Schilling et al. (1984) room temperature MAS  $^{13}\text{C}$ -NMR data for trans confirm this conclusion. They obtained the same doublets that we did and claim that doublets demonstrate resonances of the amorphous and crystalline carbons, with the amorphous carbons being slightly upfield from the crystalline carbons. Moller obtained MAS data at 27 C and also observed splitting of the methylene signal. Schilling et al. (1987) and Moller also report solid state data for trans at various temperatures above room temperature. Moller's spectra at 27 , 52 , 67 , 122 , and 134 C respectively correspond to the following states of trans: mod I, mod I, transition between mod I and mod II, mod II and melt. Note that there are a total of three methylene signals over the range of Moller's data. These signals represent the three trans states, i.e. mod I, mod II, and the amorphous melt, and are characterized by an upfield shift with increased amorphous content. Schilling et al. obtained data at 23 , 59 , 62 , and 65 C, temperatures which he claims represent mod I, the transition between mod I and mod II, the transition between mod I and mod II, and mod II. Moller suggests that the 65 data represents the transition between mod I and II while the other temperatures are various representations of mod I.

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\* Our  $^{13}\text{C}$  (solution) NMR data gave inconclusive results.

Our results are similar to the Schilling et al. (1984) room temperature data and to Moller's data at 52 C.

#### DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC was employed to determine the crystallization behavior of the homopolymers and blends of the homopolymers. In particular, the following information was monitored: 1) the melting and transition points of the homopolymers and the associated enthalpies, 2) the effect of spincasting on the melting points and enthalpies, and 3) the effect of blending for the particular case of 50/50 homopolymer blends.

Tests were performed on a Perkin-Elmer DSC4 with a Thermal Analysis Microprocessor and a Thermal Analysis Data Station (TADS). Five to 15 mg of polymer were heated and cooled in aluminum pans at specified rates. Most samples were heated at a rate of 10 C or 20 C per minute to about 30 C beyond the melt temperature. At the end of a heating trial, the samples were usually quenched from the melt to room temperature at a nominal rate of 320 C/min.

#### RESULTS AND DISCUSSION

All of the tests performed to date are listed in Table 5 along with data of prior history, heating rate, melting or other transition points, the enthalpies associated with these points, and the crystallinity fractions of the components in the samples. Crystallinity fractions were calculated using values of 24.6 cal/g for 100% crystallized syndio (Ashitaka, 1983a), and 40.6 cal/g for the transition between modifications I and II of trans (Danusso, 1966). In this report, DSC trials will be referred to by the number assigned them on the left of this table.

The melting point for the syndio homopolymer samples,  $T(s)$ , ranged from 164 C to 197 C and the crystallinity ranged from 37% to 79% where the higher percentages are for those samples tested as received from Goodyear and the lower values are generally from those that are spincast, remelted, and then quench-cooled at -320 /min. The transition between trans I and II,  $T(tI)$ , of the homopolymer samples ranged from 71 to 80 C and the mod II melting point,  $T(tII)$ , was 125 to 150 C. Trans homopolymer crystallinity based on the low temperature

transition was 40% to about 58%.

Bermudez and Fatou (1972) observed that the crystallinity of trans PBD decreased during the transition from mod I to mod II, indicating that there is not complete conversion from mod I to mod II. In our trials #15 and #16, the enthalpy of mod II increased when the temperature was held constant for ten minutes between  $T(tI)$  and  $T(tII)$ , showing that the rest of our trials, which were not held isothermally between these two temperature, definitely do not undergo complete conversion. Therefore, we recognize that calculated trans crystallinity fractions based on mod I enthalpies may be somewhat lower than the true degree of trans crystallinity.

In all of the blends, the three transitions characteristic of our homopolymers were present, two transitions for trans and one for syndio. Thus our blends were not homogeneous below 200 C and did not show any significant signs of isomorphic or eutectic behavior.

In three trials (#30, #31), blends were heated above 400 C. Beyond 280 C, oxidation and/or crosslinking occurred followed by degradation. In these trials, an endothermic shift in the baseline occurred between about 230 -255 C. This has not yet been investigated in detail but we feel that it may indicate the presence of an upper critical solution temperature (UCST) for the blends. If so, this would provide opportunities for exploring crystallization from homogeneous melts (at  $T > T_{ucst}$ ) quenched to a selected crystallization temperature. This possibility will be explored in detail in the immediate future.

In order to compare data meaningfully, we needed to determine what did or did not constitute a significant difference in results. This determination of "significant difference" was accomplished by comparing conducted at identical conditions trials. The difference between values obtained for a given parameter from identical runs was insignificant, as shown clearly in Table 6. The maximum differences observed for trials with identical conditions were 1.2 C and 0.9 cal/g. A comparison between trials #30 and #31 demonstrates that the spincasting procedure gives reproducible blends.  $T(tI)$  and  $T(s)$  values differed by less than 2 C from sample to sample. The  $T(tII)$  values differed by 6 C and were both much lower than in all of the other trials listed in Table 6, perhaps due to the low casting temperature of these two samples.  $H(tI)$  and  $H(s)$  values were within 0.1 cal/g of each other for these two samples while  $H(tII)$  values were within 0.7 cal/g..

In trials #27 and #28, all of the values are low compared to the other samples cast at 160 C. These samples had had many tests performed on them before trials #27 and #28 were conducted, and they may have become crosslinked or otherwise altered in the process. Thus the results from these trials may be unreliable but they do point out the need for concern about repeated experiments at elevated temperatures for these materials.

Two interesting categories of experiments in Table 5 lend themselves to further comparisons. Category I includes trials for samples of a given composition in which the cooling and casting histories of the samples are different but the heating rates are the same as shown in Table 7A. Category II encompasses trials of spincast samples for which the sample compositions vary. All of the groups in Category II are listed in Table 7B.

Comparisons listed in Table 7A for Category I show the effects of prior crystallization rate and of casting. Regarding crystallization history, for two samples of the same composition that were cooled at different rates, the melting points(s) and enthalpies of the sample crystallized from the melt at  $-320^{\circ}$  were less than or equal to those of a sample crystallized at a slower rate.

Casting effects on the homopolymers can be determined by comparing trials in Category I. Cast homopolymers that were quenched from the melt at  $320^{\circ}$ /min always gave lower melting points than the same uncast homopolymers quenched from the melt. The enthalpies of the cast homopolymers were less than or equal to those of the uncast materials. This result may reflect the presence of residual solvent and/or some degradation in the cast materials, although it may also reflect real differences in crystallization from solvent-based processing of these polymers.

In group IE, we can compare the results of spincasting 50/50 blends at 160 C and 120 C. We suspect that with 160 C casting, syndio crystallizes from solution at some point during the casting process, as the solvent is driven off, whereas, trans at this temperature is in the melt state and thus remains uncrystallized throughout the casting process. When the apparatus is cooled to room temperature, the trans polymer then must crystallize in the presence of syndio crystals. When processed at 120 C, which is below both melting points, syndio and trans both can crystallize during the casting process and crystallization of each component might be impeded by the other. This was apparently observed. All melting point and enthalpy values were higher for the sample cast at the higher temperature, though  $T(tI)$  was relatively constant. The crystallinity fraction of the syndio

component dropped from 0.54 to 0.44 and the trans crystallinity dropped from 0.39 to 0.26 when cast at 120 C compared to 160 C.

From groups of trials in Category II (Table 7B) we see the effect of blending on the individual components in the blend. For a given component, the melting point in the blend was always lower than that of the pure homopolymer cast under identical conditions, except for syndio PBD in Case IIC. Additionally, the enthalpy of trans (per gram of trans in sample) was lower in the blends than in the homopolymer and the syndio enthalpy in the IIA blend is less than its homopolymer enthalpy. As discussed earlier, since these samples were cast at 160 C, we suspect that the syndio crystallized from solution while the trans remained in the melt state, then when the bulk sample was cooled from 160 C, the trans also crystallized but was impeded by the presence of the syndio crystals. In case IIA, the syndio crystallinity was lower in the blend than in the homopolymer by 17% and the trans was lower by 19%. In cases IIB and IIC, the syndio enthalpy per gram of syndio was approximately equal to the enthalpy per gram of pure syndio under the same conditions, suggesting that syndio crystallization was not at all impeded by the presence of the trans chains in solution. In these cases, the crystallization of the trans was 27-28% lower in the blend than in homopolymer. In case IIA, the sample was slowly cooled in the spin caster and in cases IIB and IIC the samples were cooled at 320 C/min from the melt.

#### SUMMARY OF DSC OBSERVATIONS

Syndio homopolymer melting points ranged from 164 C to 197 C, depending on the sample history, and samples had crystallinities from 37% to 79%. The trans homopolymer mod I transition ranged from 71 C to 80 C and mod II transition from 125 C to 150 C. Crystallinity based primarily on mod I enthalpies ranged from 40% to 58%.

The homopolymers behaved in an explainable fashion with regard to cooling/heating behavior. In particular, for samples with identical prior histories, reheat rate did not affect enthalpy content at a transition point, yet the higher the heating rate, the higher the melting point. Upon reheating samples with different prior cooling histories from the melt, the samples that had been cooled more quickly had melting points and enthalpies less than or equal to the more slowly cooled samples.

The spincasting process generally resulted in lower melting point and

enthalpies than those observed for samples that had not been spincast.

In all of the blends, three transitions were present (two for trans, one for syndio). Components of the blends had lower melting points than homopolymer samples cast under the same conditions. The enthalpy of trans in the blends (per gram of trans) was ~20-30% less than in the corresponding trans homopolymer, suggesting that its crystallization was impeded by the presence of the syndio. In a slowly cooled blend, syndio crystallization was 17% less than that of the syndio homopolymer, but in quench-cooled blends, the enthalpy of the syndio was unaffected by the presence of the trans. Crystallinity fractions were lower in samples cast at 120 C, which is below both component melting points, than in samples cast at 160 C, which is below the melting point of syndio only.

#### ONGOING CHARACTERIZATION OF HOMOPOLYMERS AND BLENDS

Methanol precipitation of polymer solution followed by compression molding of the dried powder is being investigated as an alternative to spincasting. To further characterize the homopolymers and blends, wide angle X-ray scattering is being carried out. Homopolymer and blend films will also be subjected to Rheovibron testing at temperatures from -150 C to 250 C; the low-temperature data will tell us something about the nature of the amorphous regions of our samples. The postulated upper critical solution temperature (UCST), will be investigated in detail by gathering more DSC data around this point and by means of mechanical spectroscopy, light microscopy, and cloud point determinations.

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TABLE 1: POLYMORPHISM OF TRANS PBD

Authors	T(tI) oC	T(tII) oC	H(tI) cal/g	H(tII) cal/g	H(tI)/ H(tII)
Moraglio et al. (1965)	76	145	40.6	20.3	2.0
Danusso (1967)	76	145	40.6	20.3	2.0
Natta et al. (1962)	75	145	-	-	-
Bautz et al. (1981)	70	135	-	-	-
Finter and Wegner (1981)	83	164	34.6	16.6	2.1
Bermudez and Fatou (1972)	50-55	142	28.0	16.0	1.8
Dainton et al. (1962)	44	-	15.1	-	-
Kijima et al. (1976)	75-78	135-136	31.4	17.1	1.8
Stellman et al. (1973)	73	139	-	-	-
Berger and Buckley (1963)	60-65	-	-	-	-
Marchetti and Martuscelli (1976)	75	139	40.7	20.4	2.0
Mandelkern et al. (1956)	74	-	26.5	18.5	1.4
Moller (1987)	67	134	-	-	-
Iwayanagi et al. (1968)	-	148	-	-	-

TABLE 2A: IR DATA FOR SYNDIO PBD  
(values in cm-1)

this work*	Morero et al.(1960)	other sources**
662	664	662 M
667-678		667 B
		669 Z
684		
	770	
795	788	787 B
863	860	855 B
900-922	908	909 T
973		
987-1005	991	990 T
1050	1045	
1074	1070	1075 B for 1,2 s,i
1140	1131	1136 B
1220	1213	1235 E for 1,2 s,i,a
	1265	
1300	1294	1290 B for 1,2 s,i,a
1315	1310	1307 B for 1,2 s,i,a
1336	1333	1325 B for 1,2 s,i,a
1350	1343	1355 B for 1,2 s,i,a
1435	1419	
1457	1452	
1630-1646	1643	
1839	1835	
1912	1910	
1998	1989	
2130		
2280		
2330		
2520		
2570	2550	
2615		
2675	2675	
2830-3000	2847	
	2913	
	2980	
	3012	
3055-3080	3080	
3260	~3260	
3360		
3640		

\* the pen on the IR trace started early, thus these values may be up to 20 cm-1 high in the range of 600-2000 cm-1 and up to 40 cm-1 high in the range of 2000-4000 cm-1

\*\*other sources: B = Binder (1963), M = Morero et al. (1959), S = Silas et al. (1959), T = Tanaka et al. (1971), Z = Zerbi and Gussoni (1966), s = syndiotactic, i = isotactic, a = atactic.

TABLE 2B: IR DATA FOR TRANS PBD  
(values in cm-1)

this work	Morero et al. (1962)		other sources**	
	cryst	amorphous		
		764		
770	773		775	B cryst
908	910*	910*	908	W
938-978	965	965	967	B,H,No
	978		972	B cryst, S
1050			1050	He cryst
	1054		1053	B cryst
1079		1075	1054	W
			1075	He amorphous
1122	1122		1081	B
			1120	He cryst
1236	1235	1235	1230	He
			1232	No
1275			1235	B in all PBD spectra,W
1308	1312	1312	1250	B cryst
1337	1337			
1350		1351	1335	He cryst
			1350	He amorphous
1436-1450		1435	1355	B in trans and all 1,2 PBD
	1445	1450	1445	No
	1453			
1635				
1665				
1685				
1696				
1710			~1710	N
1780			~1780	N
1810				
1930	1942	1942		
1980	1984	1984		
2340 broad				
2480	2500	2500		
2520	2535	2535		
2660	2666	2666		
2825-2835	2840	2840		
2860-3020	2895			
	2915	2915		
	2950			
	2975	2975		
		3018		

\* this band reflects presence of 1,2 units

\*\*other sources: B = Binder (1963),  
H = Hampton (1949), He = Hendrix et al. (1971),  
N = Natta (1959), No = Noguchi et al. (1973),  
S = Silas et al. (1959), W = White et al. (1973).

TABLE 3: 1H-NMR DATA  
(values are in ppm)

Researchers	1,2 PBD assignments		1,4 PBD assignments		Conditions	
	[s 1,2]	>CH2	[c 1,4]	>CH2	(temp, solvent, freq)	
this work	--	2.3	5.1	--	150oC, tetralin, 250 MHz	
Ashitaka et al. (1983a)	[s 1,2]	1.33	2.29	4.97	5.58	150oC, o-DCB, 200 MHz
Zygonas et al. (1973)	[1,2]	1.2	2.2	4.8	5.5	120oC, o-DCB, 100 MHz
Senn (1963)	[1,2]	1.3	--	5.0-5.1	--	40oC, CCl4, 60 MHz
Chen (1962)	--	--	--	--	--	25oC, CCl4, 60 MHz
Tanaka et al. (1971)	[a,s 1,2]	1.20	2.10	4.95	5.40	50oC, CCl4, 100 MHz
Hatada et al. (1974)	--	--	--	--	--	35oC, CCl4, 100 MHz
Santree et al. (1973)	[1,2]	1.3	--	4.8	5.6	110oC, o-DCB, 300 MHz



TABLE 4: SOLID STATE  $^{13}\text{C}$ -NMR DATA FOR TRANS PBD  
(values are in ppm)

This work 25oC	Schilling et al. (1984)		Schilling et al. (1987)			Moller (1987)			134oC
	25oC	23oC	59oC	62oC	65oC	27oC	52oC	67oC	
33.2	--	--	--	--	--	--	--	--	32.8
34.9	33	--	34.0	34.0	34.0	--	33.4	33.4	--
	35	35.2	35.2	35.2	--	35.2	35.2	--	--
129.8	130	--	129.5	129.5	129.5	130.0	130.0	130.0	130.0
130.9	131	130.7	130.7	130.7	--	131.2	131.2	--	--

TABLE 5: DSC TRIALS

#	sample	history	heating (oC/min)	transition temps (oC)		enthalpies (cal/g)		H(tI)/ H(tII)	H(tI)*/ H(tI)**	H(s)*/ H(s)**
1	syndio	as received	+20		193					0.78
2	syndio	as received	+10		193					0.79
3	syndio	cooled melt, -320o/min	+10		193					0.39
4	syndio	cooled melt, -320o/min	+20		194					0.44
5	syndio	crystallized from melt	-20		155					0.52
6	syndio	cast 155oC,								
		cooled 3hr to 25oC	+20		197					0.65
7	syndio	cast 155oC,								
		cooled melt, -320o/min	+20		187					0.39
8	syndio	cast 155oC,								
		cooled melt, -320o/min	+10		183					0.37
9	trans	as received	+10	63	150					
10	trans	cooled melt, -320o/min	+10	74	141					
11	trans	cooled melt, -320o/min	+10	74	140					
12	trans	cooled melt, -320o/min	+20	76	141					
13	trans	cooled melt, -320o/min	+20	77	140					
14	trans	cooled melt, -20o/min	+50	80	144					
15	trans	cooled melt, -20o/min,	+20							
		held at 90o for 10min			141					
16	trans	cooled melt, -20o/min,	+20							
		held at 90o for 20min	+20		141					
17	trans	crystallized from melt	-20	48	120					
18	trans	crystallized from melt	-20		120					
19	trans	crystallized from melt	-20		119					
20	trans	crystallized from melt	-50	25	115					
21	trans	cast 160oC,	+20	77	131					
		cooled 3hr to 25oC								
22	trans	cast 160oC,	+20							
		cooled melt, -320o/min	+20	74	126					
23	trans	cast 160oC,	+10	73	125					
		cooled melt, -320o/min	+20	72	129					
24	50/50	cast 160oC,								
		cooled 3hr to 25oC	+20		194					
25	50/50	cast 160oC,	+20	70	123					
		cooled melt, -320o/min	+20	70	123					
26	50/50	cast 160oC,	+10	70	123					
		cooled melt, -320o/min	+20	64	103					
27	50/50	cast 160oC,								
		cooled melt, -320o/min	+20		164					
28	50/50	cast 160oC,	+20							
		cooled melt, -20o/min	+20		164					
		held at 90o for 10min			107					
29	50/50	cast 160oC,	-20							
		crystallized from melt			126					
30	50/50	cast 120oC on 12/8/87	+20	73	102					
		cooled 3hr to 25oC								
31	50/50	cast 120oC on 11/22/87	+20	74	108					
		cooled 3hr to 25oC								

\* enthalpy per gram of component, not total sample

\*\*theoretical enthalpy of 100% crystallized sample

^ value based on H(tII) enthalpies

TABLE 6: TRIAL COMPARISONS FOR ERROR DETERMINATION

sample	history	heating (oC/min)	transition T(tI)	transition temps (oC) T(tII)	enthalpy (cal/g) H(tI)	enthalpy (cal/g) H(tII)	#
trans	cooled melt, -320o/min	+10	74	141	20.5	8.0	10
			74	140	20.6	8.0	11
trans	cooled melt, -320o/min	+20	76	141	21.7	7.8	12
			77	140	21.3	8.7	13
trans	crystallized from melt	-20	48	120	-17.6	-7.8	17
			--	120	--	-8.1	18
			--	119	--	-8.4	19

TABLE 7A: CATEGORY I, TRIALS WITH VARIED COOLING AND CASTING HISTORIES

sample	history	heating (oC/min)	transition temps (oC)		enthalpies (cal/g)		H(tI)*/ H(tI)**	H(s)*/ H(s)**	#
			T(tI)	T(tII)	H(tI)	H(tII)			
IA syn	as received	+10						0.79	2
	cooled melt, -320o/min	+10						0.39	3
	cast 155oC,								
IB syn	cooled melt, -320o/min	+10						0.37	8
	as received	+20							
	cooled melt, -320o/min	+20						0.78	1
	cast 155oC,							0.44	4
IC trans	cooled 3hr to 25oC	+20							
	cast 155oC,							0.65	6
	cooled melt, -320o/min	+20							
								0.39	7
ID trans	as received	+10	63	150					
	cooled melt, -320o/min	+10	74	141				0.58~	9
	cooled melt, -320o/min	+10	74	140	20.5	8.0		0.51	10
	cast 160oC,				20.6	8.0		0.51	11
	cooled melt, -320o/min	+10	73	125	18.0	8.1		0.44	23
IE 50/50	cooled melt, -320o/min	+20	76	141	21.7	7.8		0.53	12
	cooled melt, -320o/min	+20	77	140	21.3	8.7		0.53	13
	cooled melt, -20o/min,	+20							
	held at 90o for 10min,								
	cooled melt, -20o/min,	+20						0.52~	15
	held at 90o for 20min,								
IE 50/50	cast 160oC,	+20	77	131	19.5	8.8		0.48	16
	cooled 3hr to 25oC								
	cast 160oC,	+20	74	126	18.5	7.7		0.54~	21
	cooled melt, -320o/min							0.46	22
	cast 160oC,	+20	70	123	6.7	2.7		0.33	25
	cooled melt, -320o/min								
	cast 160oC,	+20	72	129	7.9	3.8		0.39	24
	cooled 3hr to 25oC								
	cast 120oC on 12/8/87	+20	73	102	5.3	2.1		0.26	30
	cooled 3hr to 25oC								
	cast 120oC on 11/22/87	+20	74	108	5.3	2.7		0.44	31
	cooled 3hr to 25oC								



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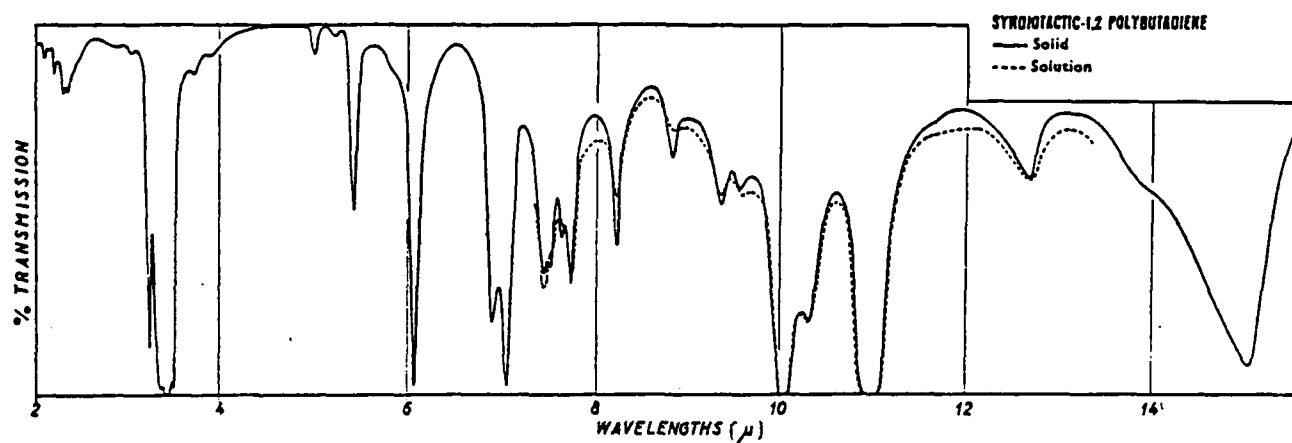
Figure 1: IR Spectra for Syndio PBD

Figure 2: IR Spectra for Trans PBD

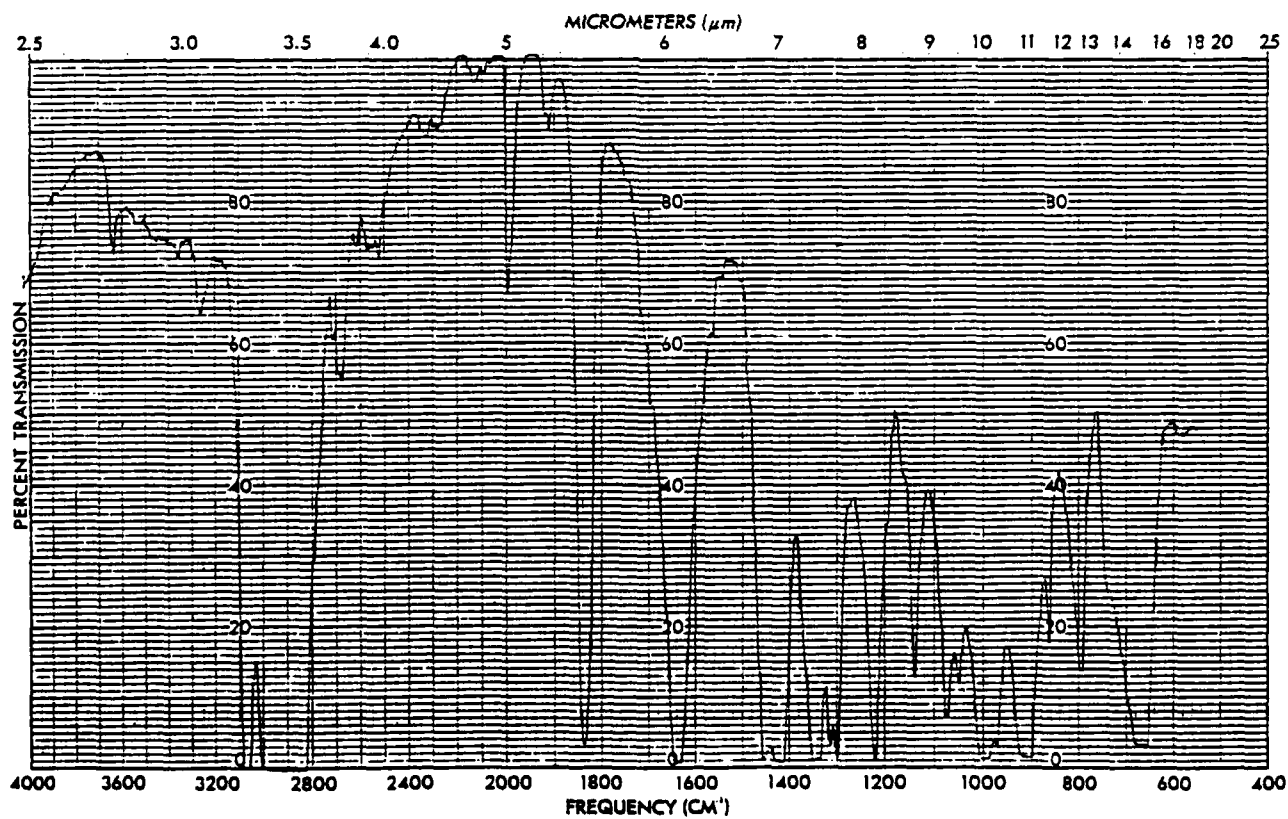
Figure 3:  $^1\text{H}$ -NMR Spectra

Figure 4: Solid State MAS  $^{13}\text{C}$ -NMR Spectra

Figure 1: IR Spectra for Syndio PBD

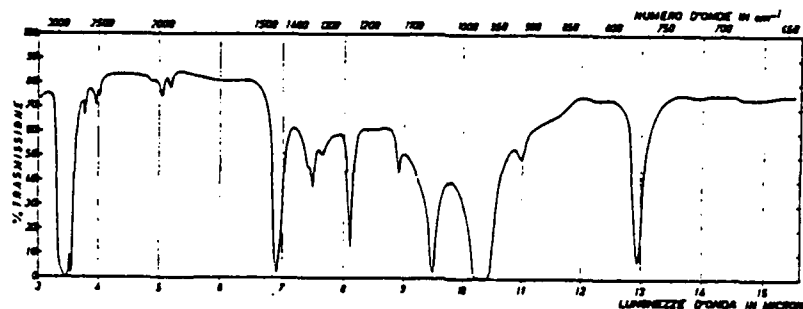


1a. Morero et al. (1960)

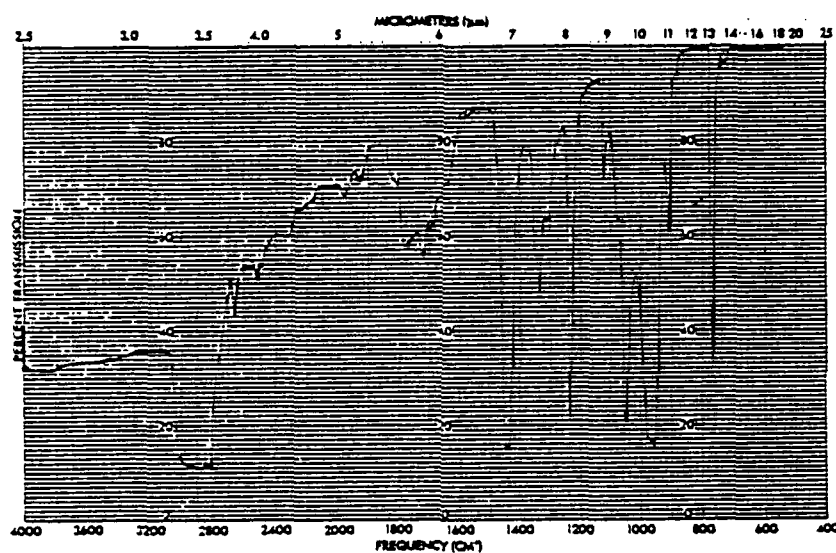


1b. Goodyear sample

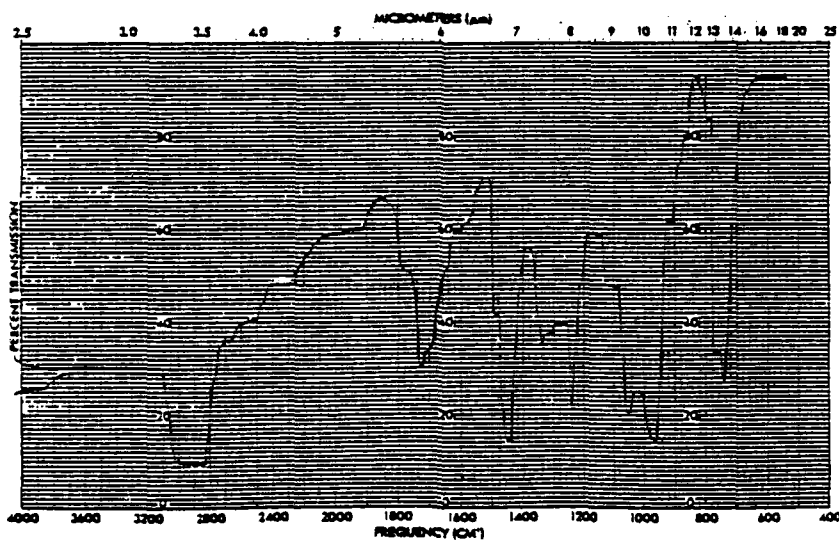
Figure 2: IR Spectra for Trans PBD



2a. Morero et al. (1962)



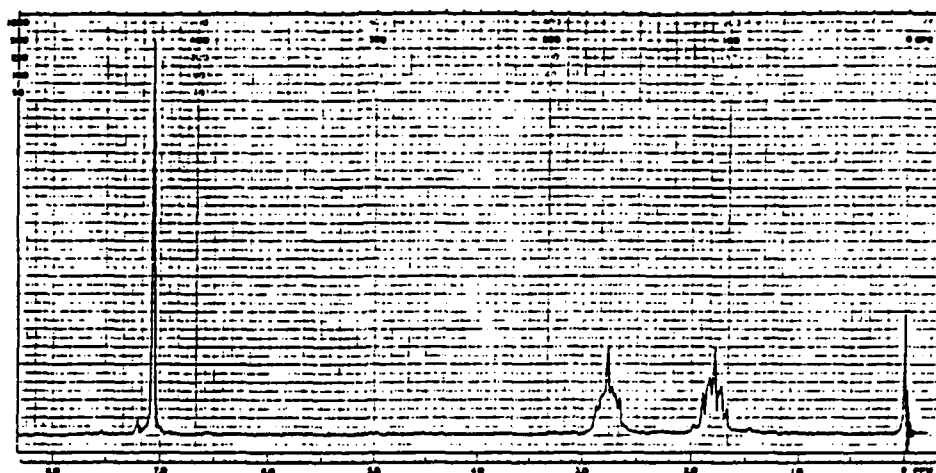
2b. Goodyear sample



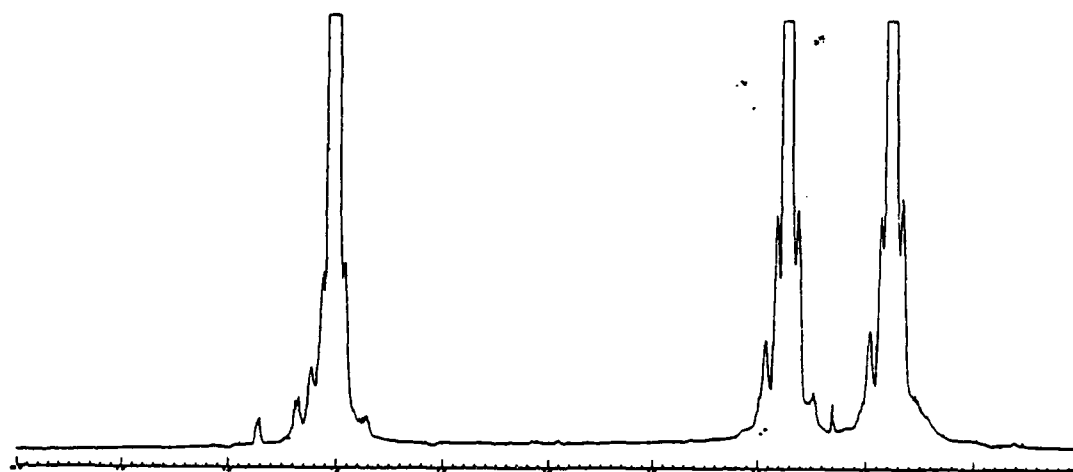
2c. cast Goodyear sample



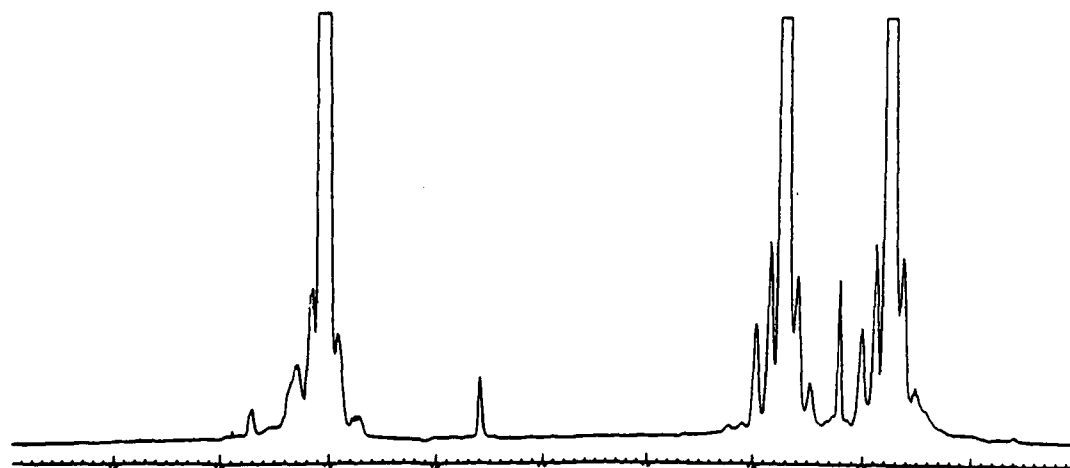
Figure 3:  $^1\text{H}$ -NMR Spectra



3a. Tetralin

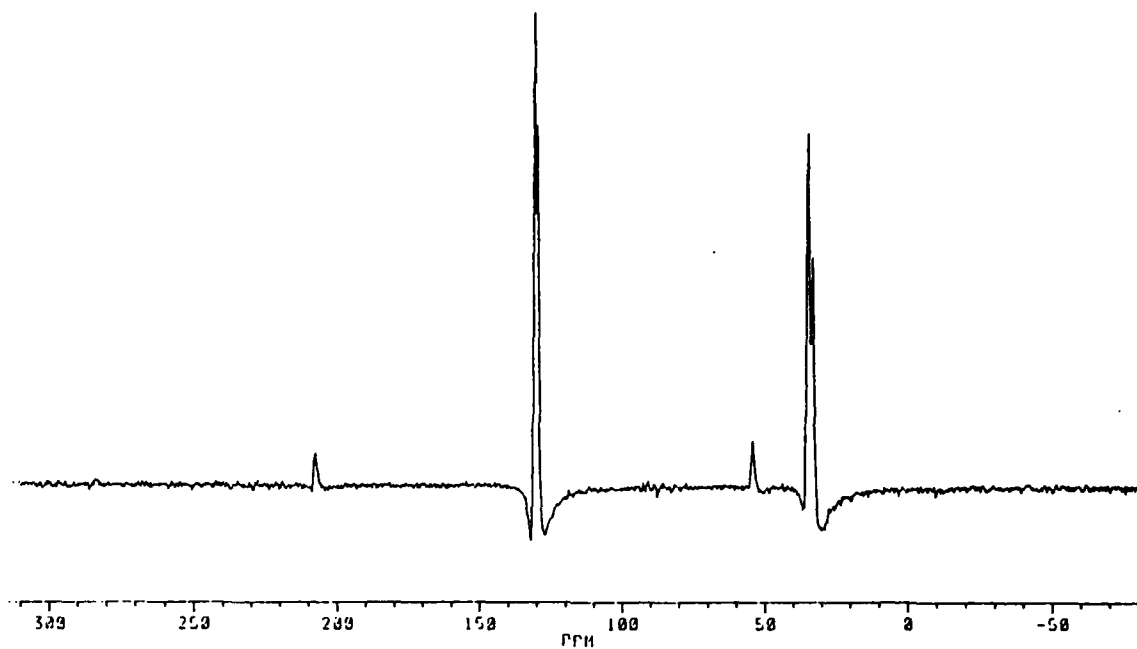


3b. Syndio PBD

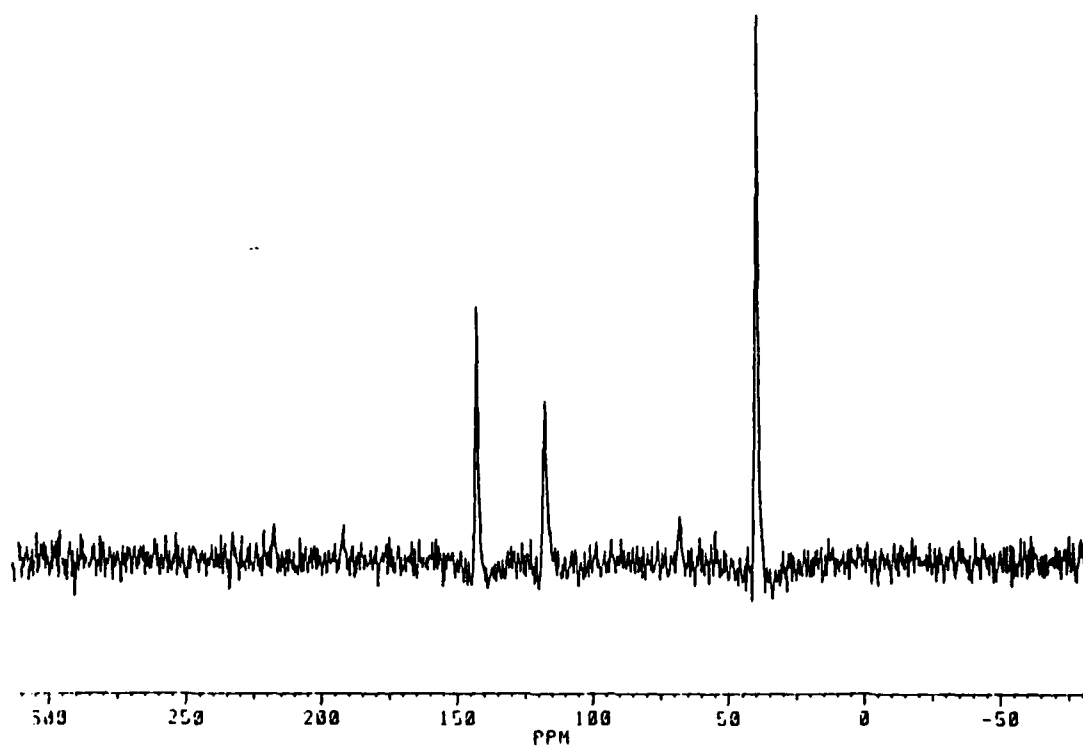


3c. Trans PBD

Figure 4: Solid State MAS  $^{13}\text{C}$ -NMR Spectra



4a. Syndio PBD



4b. Trans PBD

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